High-Viscosity Reference Liquids at High Pressures

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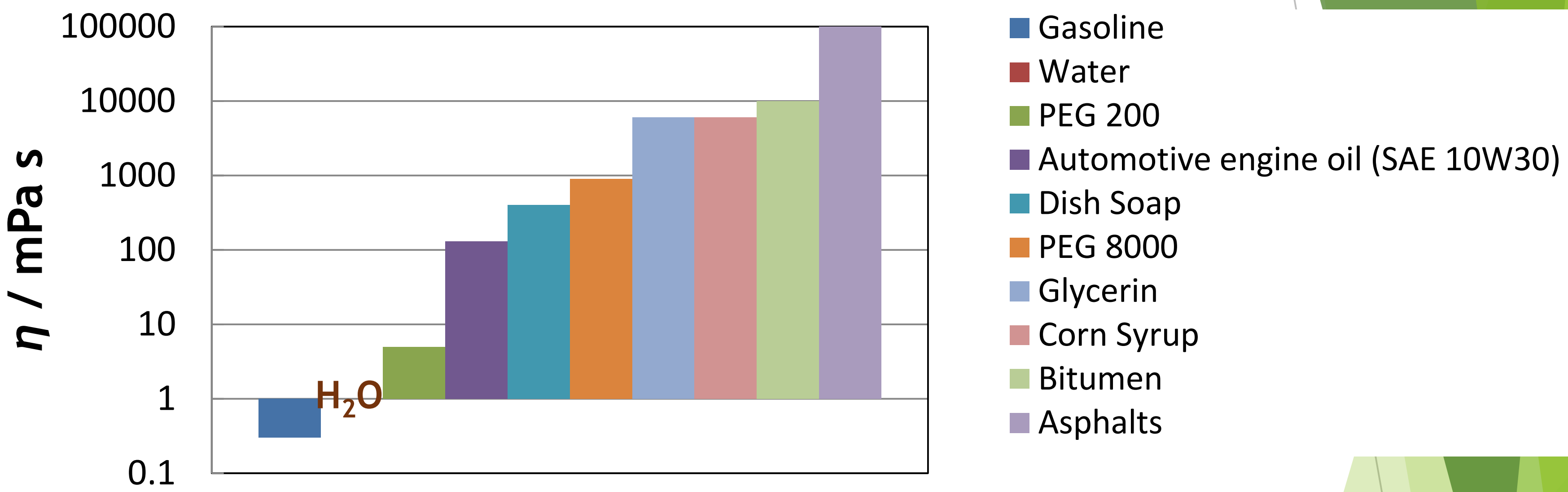
The need for Viscosity Reference Liquids

- The viscosity of fluids can differ by a factor of 10^{14}



- Usually instruments need calibration:
  - Over viscosity, temperature and pressure.
- Reference Liquids for High Viscosity are Required by the Industry

Viscosity Reference Liquids

- Primary Reference
  - Water is the only one primary reference for viscosity
  - η = 1.0016 mPa s ± 0.25 %, T = 293.15K, p = 0.1 Mpa

    (Swindells et al., 1954, NBS / NIST)
- Secondary Reference
  - Reference data traceable to the primary reference
- Working or Industrial Reference
  - Calibrate/verify the viscosity/performance of instruments;
  - Quality control;
- Commercially available Industrial References are very useful, however they have several limitations
  - expiration date;
  - expensive;
  - limited T range;
  - 0.1 MPa data only;
  - can be used only once.

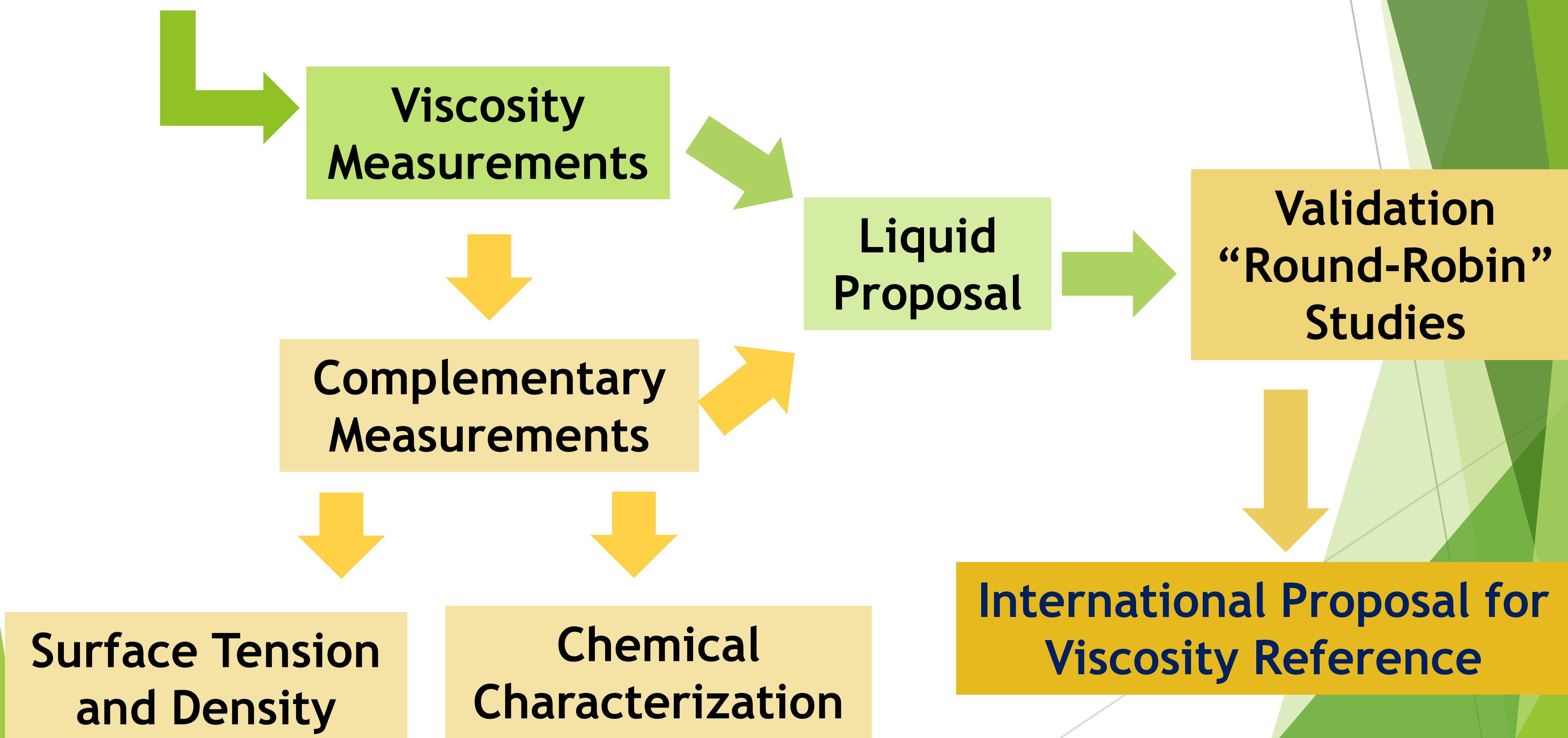
Viscosity Reference Liquids

- Commercially available Industrial Reference Fluids – (primary reference traceable)
  - Viscosity standards → hydrocarbon and silicone oils
  - For lower viscosity → mineral oils and polyalphaolefins
  - Polybutenes are used as high viscosity standards
    - Cannon and Brookfield (traceable by NIST)
    - ZMK (traceable by PTB)
- Why do we need calibrants beyond water?
  - Sometimes water is inappropriate to use in the calibration of certain types of equipment for viscosity measurement
  - Although water is the primary reference for viscosity
    - Large differences between the water properties and liquids of interest can cause problems in calibrations

Validation of Industrial Viscosity Reference Liquids

Liquid Selection

- thermally stable;
- easily obtained/widely available at specified purities;
- environmentally safe and friendly;
- high chemical stability;

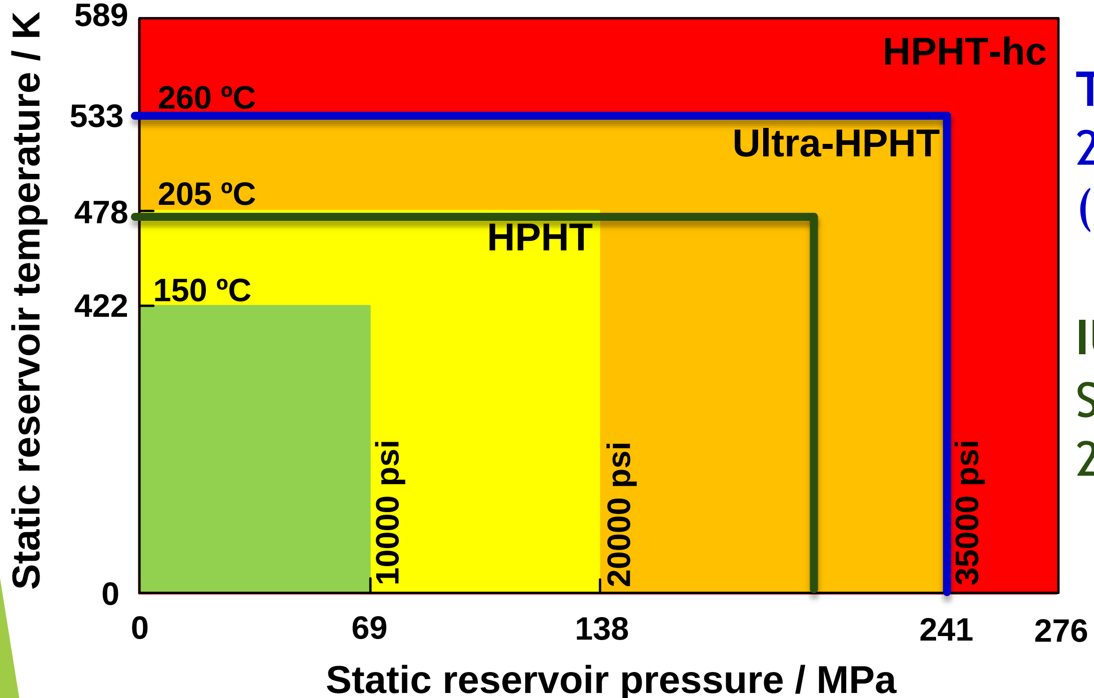


Viscosity Reference Liquids

Goals and International Projects for Viscosity Reference Liquids	
IUPAC project (No. 2002-005-1-100) ***Started: 2003; Ended 2009*** Thermodynamics of ionic liquids, ionic liquid mixtures, and the development of standardized systems U= ±(2 - 5)%	**IATP project; Started 2008;** ***Still Running*** High-temperature, high-pressure viscosity standards. J.M.N.A. Fareleira, F.J.P Caetano (PT), W. A. Wakeham, J.P.M. Trusler (UK), A.P. Froba, A. Leipertz, B. Rathke (DE), K. Harris (Aus), A.R.H. Goodwin, A. Laesecke (USA), J. Fernandez (ES), K. Schmidt (CA), Chr. Boned (FR)
IATP project; Started 2008; ***Still Running*** Round Robin project on ionic liquids viscosity and thermal conductivity measurements. C.A. Nieto de Castro, J.M.N.A. Fareleira (PT); A. Leipertz , A. Froeba, U. Hammerschmidt, B. Rathke (DE); J. Fernandez (ES), R. Perkins (USA), and K. Harris (Au).	Proposed to IATP in 2010 20 mPa.s, 241 MPa, 533 K (deepwater – Gulf of Mexico) 1000 mPa.s , 10 MPa, 473 K (surface – Canada) U= ±5% acceptable; U= ±2% desirable
IUPAC project (No. 2012-051-1-100) *Started in 2013; Still Running* **20 mPa.s, 200 MPa, 473 K** U= ±5%	High Viscosity High Pressure High Temperature

Viscosity Reference Liquids - Alternatives

- International Goals and Projects for Viscosity Reference Liquids



[1] HPHT classification system. The classification boundaries represent stability limits of common well-service-tool components—elastomeric seals and electronic devices.

Target proposed to IATP in 2010:
20 mPa.s, 241 MPa, 533 K
(deepwater)

IUPAC project **(No. 2012-051-1-100)**
Started in 2013; Still Running
20 mPa s, 2000 bar, 473 K

Viscosity Reference Liquids

- Liquids proposed as industrial references for viscosity under the guidance of IUPAC and IATP

Liquid	η[(a)] (mPa s)	T range (K)	p range (MPa)	η range (mPa s)	U (%)	Min Purity (%)	year
Cyclopentane[1]	0.416	220-310	0.1-25	0.4-1.5	0.2-1.6	99	2004
Toluene[2,3]	0.555	213-400	0.1-250	0.2-3	0.2-3	99	2001; 2006
Diesels, biodiesels, low molecular weight polymers and light oils							
Squalane[4,5]	28.2	273-473	0.1-200	0.85-954	1-5	98	2013; 2014
[C_6mim][NTf_2][6,7]	69.4	258-433	0.1	2.95-967.6	0.5-5	99.5	2009
DIDP[8]	88.5	288-308	0.1	49.3-179.8	0.3-2	99.8	2008
Heavy oils and high molecular weight polymers							

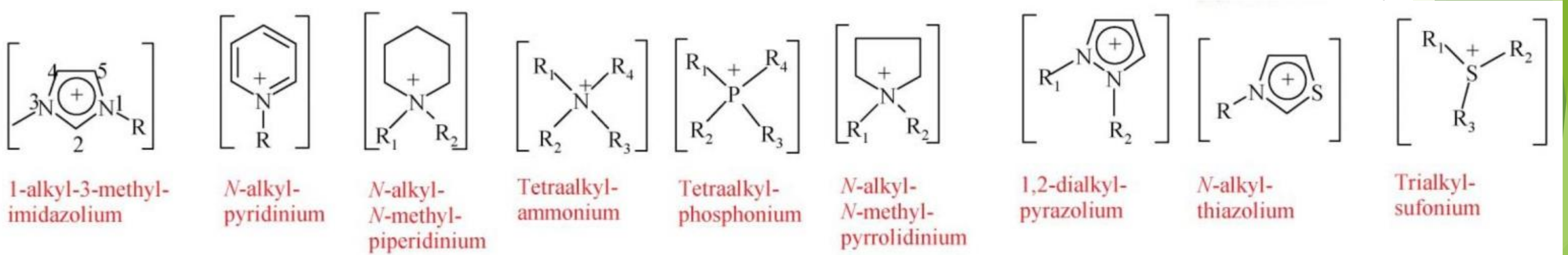
(a) 298 K and 0.1 MPa

Low Viscosity

Moderately High Viscosity

Ionic Liquids as Viscosity References

- Possible application areas
  - Electrochemistry
  - Physical chemistry
  - Biological uses
  - Analytics
  - Solvents and catalysts
  - Engineering
- Viscosity depends essentially on Cations



- Hydrophobicity essentially depends on Anions

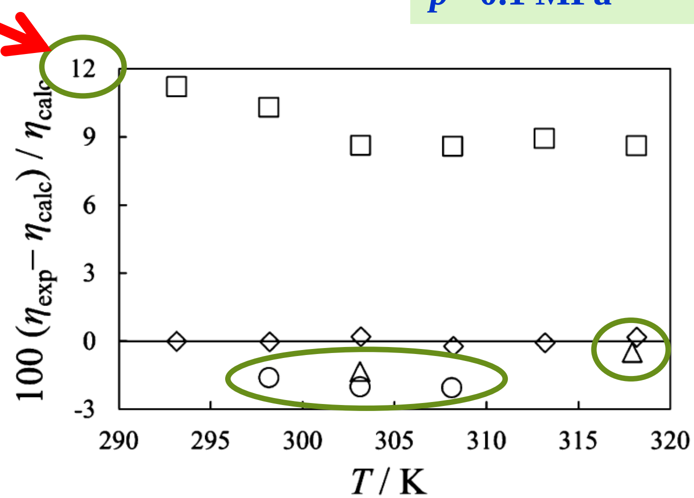
water-immiscible	→	water-miscible
$[PF_6]^-$	$[BF_4]^-$	$[CH_3CO_2]^-$
$[NTf_2]^-$	$[OTf]^-$	$[CF_3CO_2]^-$, $[NO_3]^-$
$[BR_1R_2R_3R_4]^-$	$[N(CN)_2]^-$	Br^-, Cl^-, I^-
		$[Al_2Cl_7]^-$, $[AlCl_4]^-$ (decomp.)

Vibrating Wire Method – ILs Tests

[P$_{6,6,6,14}$][dca] ; *U*=±2 %

(0.04 S.m^{-1}; 323 K)

T= 298.2 K
η= 378 mPa.s
p= 0.1 MPa



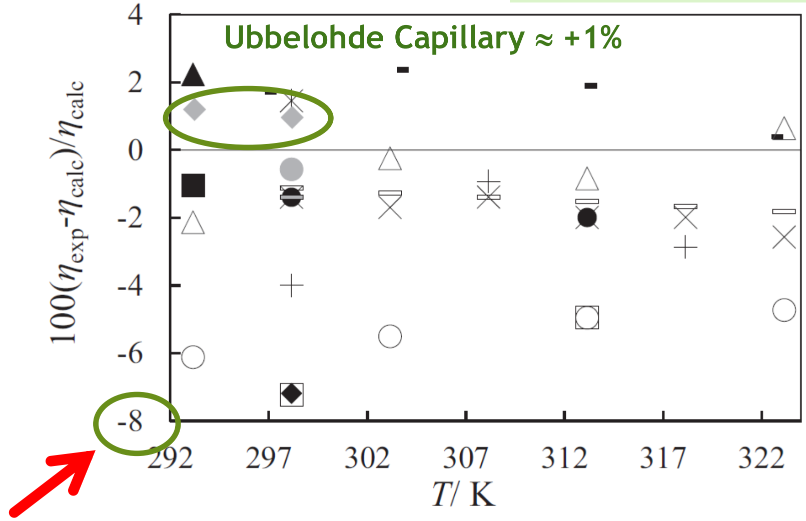
Deviations of the viscosity results for [P$_{6,6,6,14}$][dca], obtained by Pereiro et al.,[33] □, and in the present work using: the vibrating wire technique, ◇ (nominal values from Table 6); an Ubbelohde capillary, ○, and an Ubbelohde microcapillary, △, from the correlation eq 10 with the parameters of Table 5.

H_2O_{VW} -> (53 - 300) ppm
$H_2O_{micro-Ubb.}$ -> 379 ppm, aft. meas.
$H_2O_{Ubb.}$ -> 247 ppm, aft. meas.

[C$_2$mim][EtSO$_4$] ; *U*=±2 %

(0.4 S.m^{-1}; 298 K)

T= 298.2 K
η= 98.6 mPa.s
p= 0.1 MPa

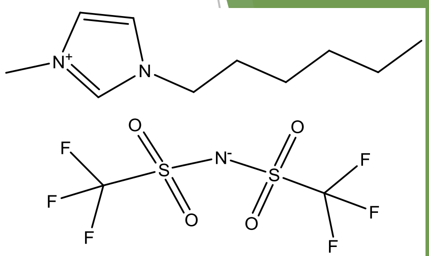


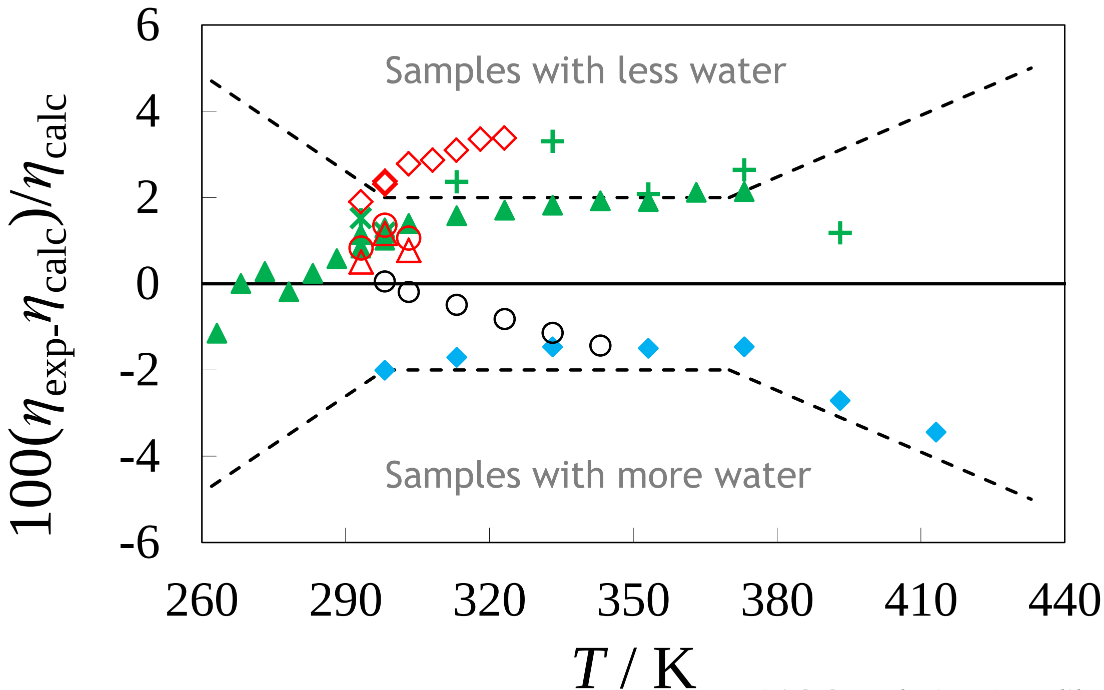
Deviations from the correlation Eq. (6) of viscosity results for [C$_2$mim][EtSO$_4$] of literature data: Diogo et al. [10] (◆); Jaquemim et al. [28] (▬); Gómez et al. [35] (×); Rodrigues and Brennecke [38] (+); Arce et al. [27] (⚹); Gonzalez et al. [42] (●); Fröba et al. [32] (▲, SLS); Fröba et al. [32] (■, rotational viscometer); Calvar et al. [48] (▬); Torrecilla et al. [38] (♦); Fröba et al. [40] (△); Fernandez et al. [39] (○); McHale et al. [47] (●); Torrecilla et al. [50] (□) and Gaciño et al. [51] (▭).

H_2O -> (6 - 7) ppm
$H_2O_{Ubb.}$ -> (27 - 65) ppm

Ionic Liquids as Standards for Viscosity

- [C$_6$mim][NTf$_2$]; η = 68 mPa.s at 273 K and 0.1 MPa
- Water content: 10 to 410 ppm





Comparisons of our VW data (symbols in red) with data obtained with drier samples is better than 1.6%

Methods (-3.4% to +3.4%):
- *Vibrating wire;*
- *Ubbelohde capillary;*
- *Ostwald capillary;*
- *Rotational: Stabinger;*

— **IUPAC Correlation (Kandil et al, Widegren and Magee, Santos et al viscosity data)**

◆ **Kandil et al.**: vibrating-wire, sample A – 43 to **410** ppm
+ **Kandil et al.**: vibrating-wire, sample B – 7 to **117** ppm
✱ **Widegren and Magee.**: Ubbelohde capillary, **10** (298.15 K) and **20** ppm (293.15 K)
▲ **Widegren and Magee.**: Anton Paar SVM 3000, **10** ppm
○ **Santos et al.**: Ostwald capillary, 119 to **196** ppm
◇ **IST**: vibrating-wire, 25 to **89** ppm
△ **IST**: Ubbelohde Capillary, 44 to **221** ppm
○ **IST**: Micro-Ubbelohde Capillary, 44 to **210** pm

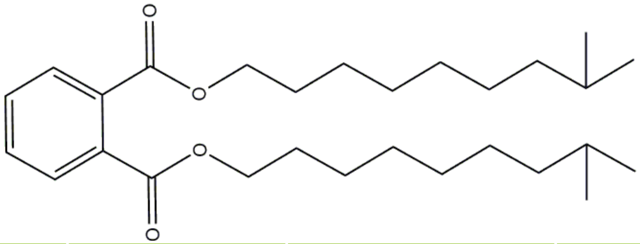
- When considering all published data, deviations from (-16 to +16)% from the IUPAC correlation are obtained

Ionic Liquids as Viscosity References – Remarks

- Viscosity of ILs can be considerably affected by water:
  - 100 ppm of water can decrease viscosity by 1 to 1.5%
  - it has been indicated that small quantities (tens to few hundreds ppm) of other contaminants like halides can affect significantly the viscosity
- Difficult to achieve viscosity differences within ±2% in Round-Robin studies
- In the Uncertainty determination of the Viscosity, water content must be accounted - not only calibration or experimental uncertainty.
- The water contents must be reported - after or before and after viscosity measurements; halides content should also be reported;
- Surface tension effect on capillary viscosity measurements is neglected by the majority of the authors
- Electrical conductivity effect of the liquid could affect the accuracy of some viscosity measurement methods

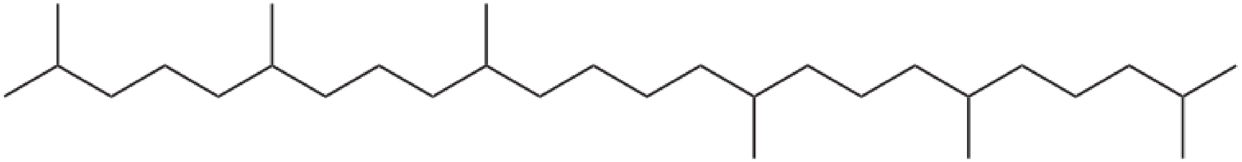
Viscosity Reference Liquids

- Diisododecyl Phthalate, DIDP (Plasticizer)
- Disadvantage:
  - mixture of isomers;
  - discontinued.



Liquid	η[(a)] (mPa s)	T range (K)	p range (MPa)	η range (mPa s)	U (%)	Min Purity (%)	year
DIDP[3]	88.5	288-308	0.1	49.3-179.8	0.3-2	99.8	2008

- Squalane
- Disadvantage:
  - viscosity to low for the high viscosity goals

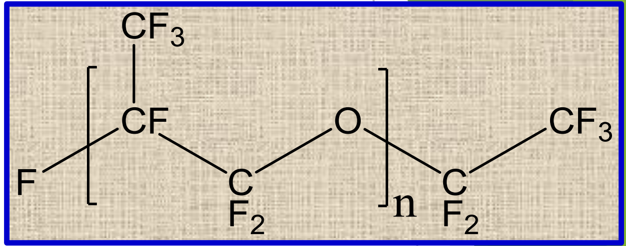


Liquid	η[(a)] (mPa s)	T range (K)	p range (MPa)	η range (mPa s)	U (%)	Min Purity (%)	year
Squalane[4,5]	28.2	273-473	0.1-200	0.85-954	1-5	98	2013,2014

Liquids Suitable to be Viscosity Standards at High Pressure

- **Moderately high to High Viscosity:** Krytox® (DuPont patent)
  - Properties:
    - Low vapor pressure;
    - Low and high temperature resistant;
    - Non toxicity;
    - High resistance to biodegradability;
    - Chemical inert;
    - high boiling point;
    - Doesn't burn.
  - Main application: lubricants;
  - Liquid range: (-75 to 350) ºC;
  - Purity >99 % (up to 99.9%)

A Polymer



Perfluoropolyether Oils

Krytox ® GPL	~n (average)	MW (average) / kg.mol^{-1}	~Viscosity (293 K) / mPa.s
100	5	0.96	13.3
101	6	1.18	30.4
102	10	1.72	68.4
103	13	2.28	152
104	18	3.15	342
105	28	4.73	1045
106	35	5.94	1539

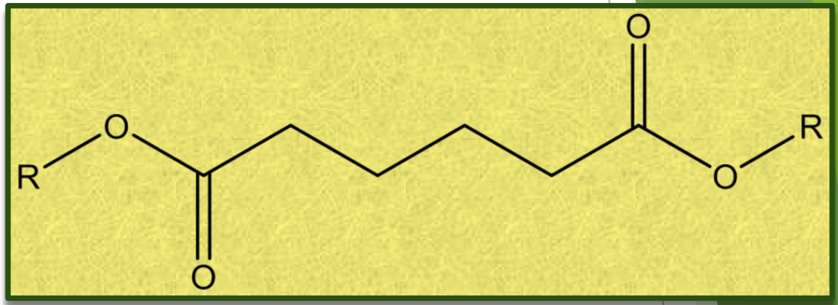
Viscosity reference liquids

- Liquids proposed as industrial references for viscosity under the guidance of IUPAC with IATP

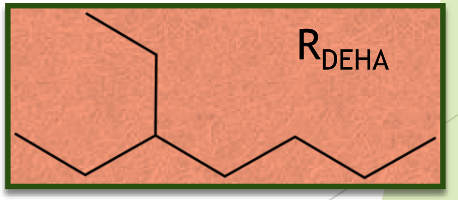
Liquid	η[(a)] (mPa s)	T range (K)	p range (MPa)	η range (mPa s)	U (%)	Min Purity (%)	year
cyclopentane	**0.416**	220-310	0.1-25	0.4-1.5	0.2-1.6	99	2004
Toluene[1,11]	**0.555**	213-400	0.1-250	0.2-3	0.2-3	99	2001; 2006
				Dialkyl Adipates			
Squalane[4,5]	**28.2**	273-473	0.1-200	0.85-954	1-5	98	2013, 2014
$[C_6mim][NTf_2]$	**69.4**	258-433	0.1	2.95-967.6	0.5-5	99.5	2009
DIDP[12]	**88.5**	288-308	0.1	49.3-179.8	0.3-2	99.8	2008
				Trimillitates			

Liquids Suitable to be Viscosity Standards at High Pressure

- **Low Viscosity:** Dialkyl Adipates
  - Properties:
    - low vapor pressure;
    - low temperature resistant;
    - low viscosity;
    - low toxicity;
    - high biodegradability;
    - high boiling point

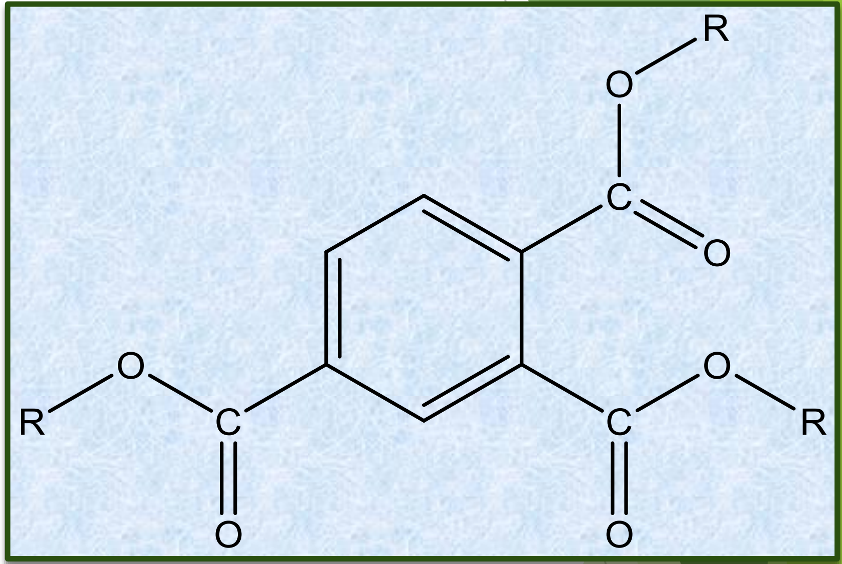


  - Large application: plasticizers; solvents; lubricants; corrosion protection; pigment dispersant.
  - Liquid range: (-30 to 200) °C; Purity 99 %
    - Dimethyl Adipate
    - Diethyl Adipate
    - Dipropyl Adipate
    - Dibutyl Adipate
    - Diisobutyl Adipate
    - Bis(2-Ethylhexyl) Adipate

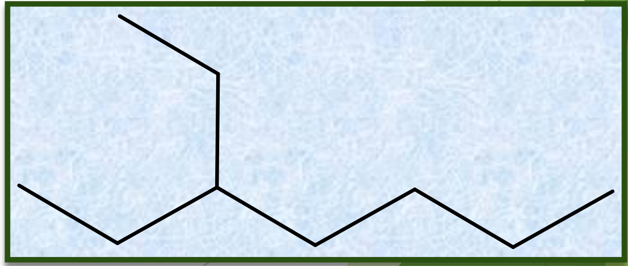


Liquids Suitable to be Viscosity Standards at High Pressure

- **High Viscosity:** Trimillitates
  - Properties:
    - low vapor pressure;
    - low temperature resistant;
    - high temperature resistant;
    - high viscosity;
    - low toxicity;
    - high boiling point



  - Aplications: plasticizers; high temperature polymers.
    - Tris(2-Ethylhexyl) Trimellitate - TOTM
      - Purity 99 %
      - Liquid range: (-50 to 414) ºC



New vibrating wire sensor

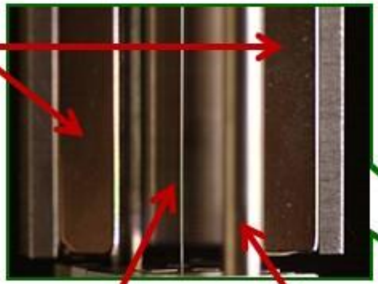
- 1 - top washers;
- 2 - upper claw chucks;
- 3 - vibrating wire;
- 4 - rod spacers;
- 5 - inferior claw chucks;
- 6 - superior rod clamping;
- 7 - magnetic circuit;
- 8 - magnets;
- 9 - inferior rod clamping,
- 10 - bottom washers

Newtonian viscosity standard (NVS) 20 AW (PTB) used to calibrate the VW sensor

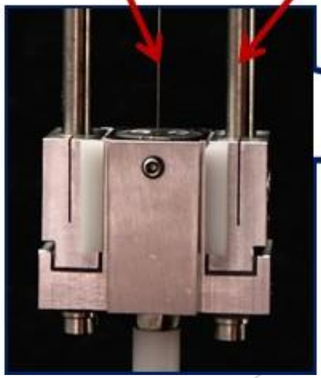
NVS 20 AW, 298.15 K;

η = 16.02 mPa.s.

Viscosity range: up to about 460 mPa.s
Wire material: tungsten
Vacuum frequency: about 1.0 kHz
R_{wire} = 150 μm
Viscosity U% = ±(2-3)



Open magnetic circuit



Without magnetic circuit

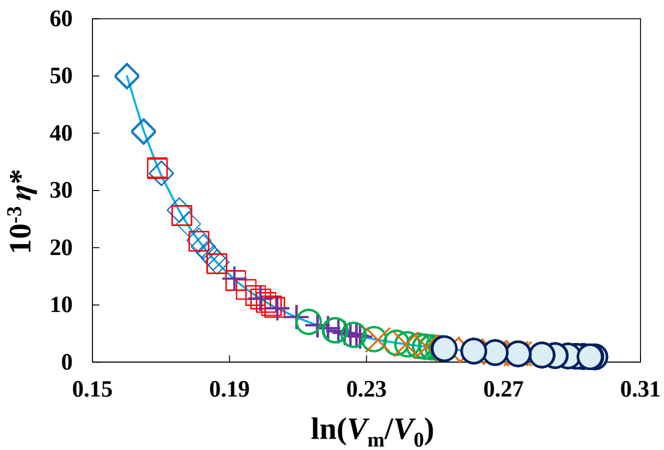
(TOTM) Tris(2-ethylhexyl) trimellitate - results

Viscosity range (mPa.s)	Temperature (K)	Pressure (MPa)
9 – 460	303 - 373	up to 65

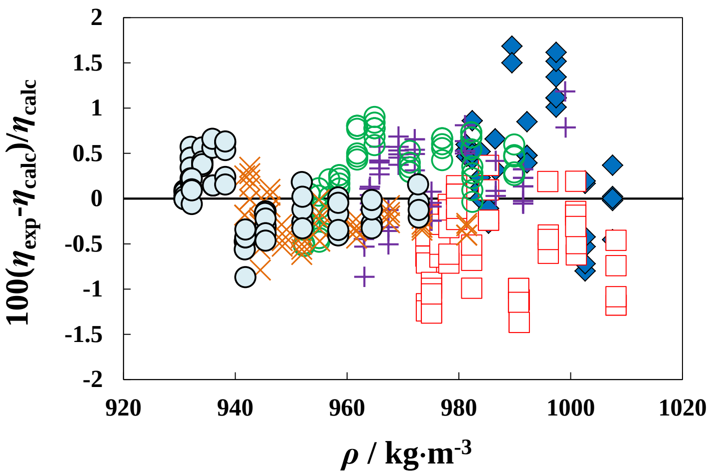
- viscosity data of TOTM were correlated with density using a semi-empirical method, a heuristic development of the kinetic theory for dense hard-sphere fluids, applied to the van der Waals model of a liquid

$$\eta^* = 6.035\times10^{8}\left(\frac{1}{MRT}\right)^{1/2}\eta\,(V_{\mathrm{m}})^{2/3} \qquad \frac{1}{\eta^*}=\sum_{\mathrm{i}=0}^{4}a_{\mathrm{i}}\left(\frac{V_{\mathrm{m}}}{V_0}\right)^{\mathrm{i}} \qquad V_0\times10^{6}\,/\,(\mathrm{m}^3\ \mathrm{mol}^{-1}) = l + mT + nT^2$$

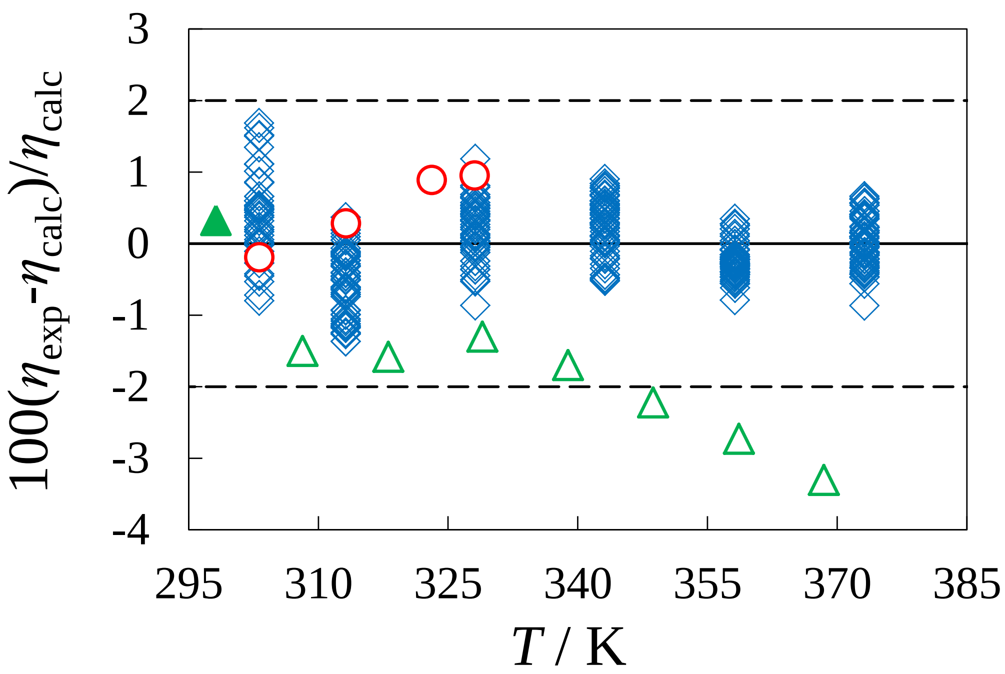
◆ 303 K □ 313 K + 328 K ○ 343 K × 358 K ○ 373 K



Statistical parameters of correlation	
rmsd /%	0.53
bias /%	0.00
MaxDev %	+1.7



(TOTM) Tris(2-ethylhexyl) trimellitate - comparisons



—— **TOTM Hard Spheres Correlation**

◇ **IST 2014 (*U*=±(2-3)%)**: vibrating-wire, water content - 99 to **175** ppm

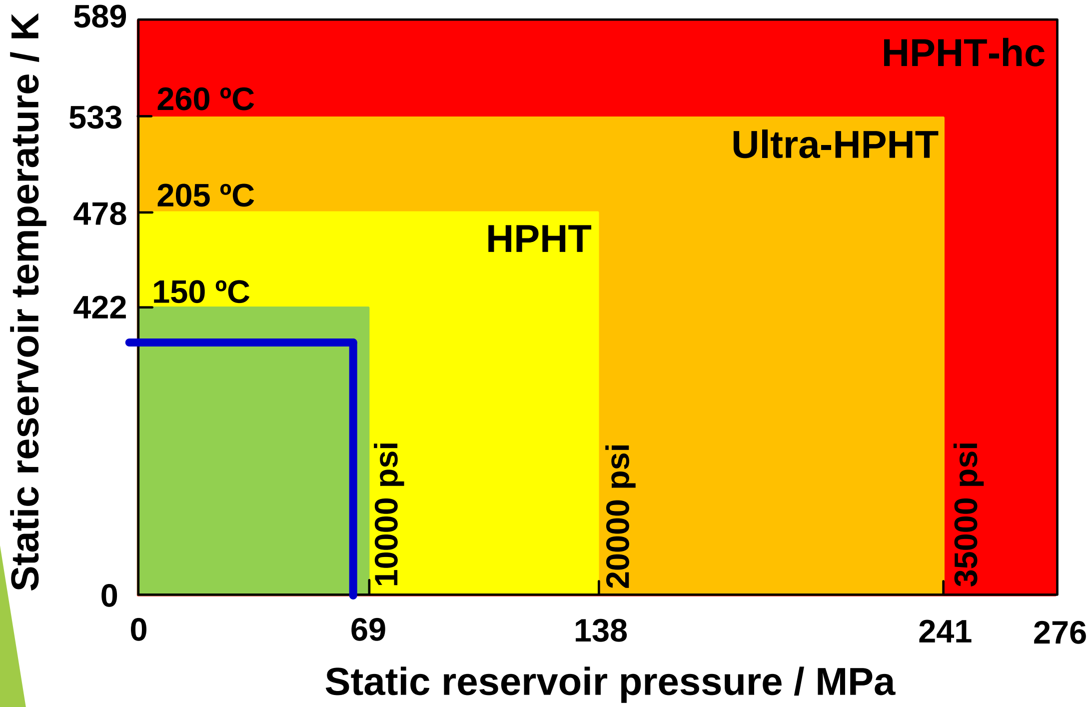
○ **IST 2014 (*U*=±1.5%)**: Ubbelohde Capillary, water content - 26 to **248** ppm (TOTM VW correlation extrapolated for 0.1MPa)

△ **Lorenzi et al 1998 (*U* not reported)**: Ubbelohde Capillary (TOTM VW correlation extrapolated for 0.1MPa)

▲ **Lorenzi et al 1998 (*U* not reported)**: Ubbelohde Capillary (TOTM VW correlation extrapolated for 0.1MPa and to 298 K)

New Viscosity Measurements of New Suitable Liquids for Reference Viscosity

- Dialkyladipates
- Trialkyl Trimellitates
  - High Pressure VW Viscosity Measurements



DMA
DBA
DPA
TOTM

p_{range}: 1 - 65 MPa
T_{range}: 293 - 373 K

η_{range}: (1.1 - 464) mPa.s

Viscosity Reference Liquids

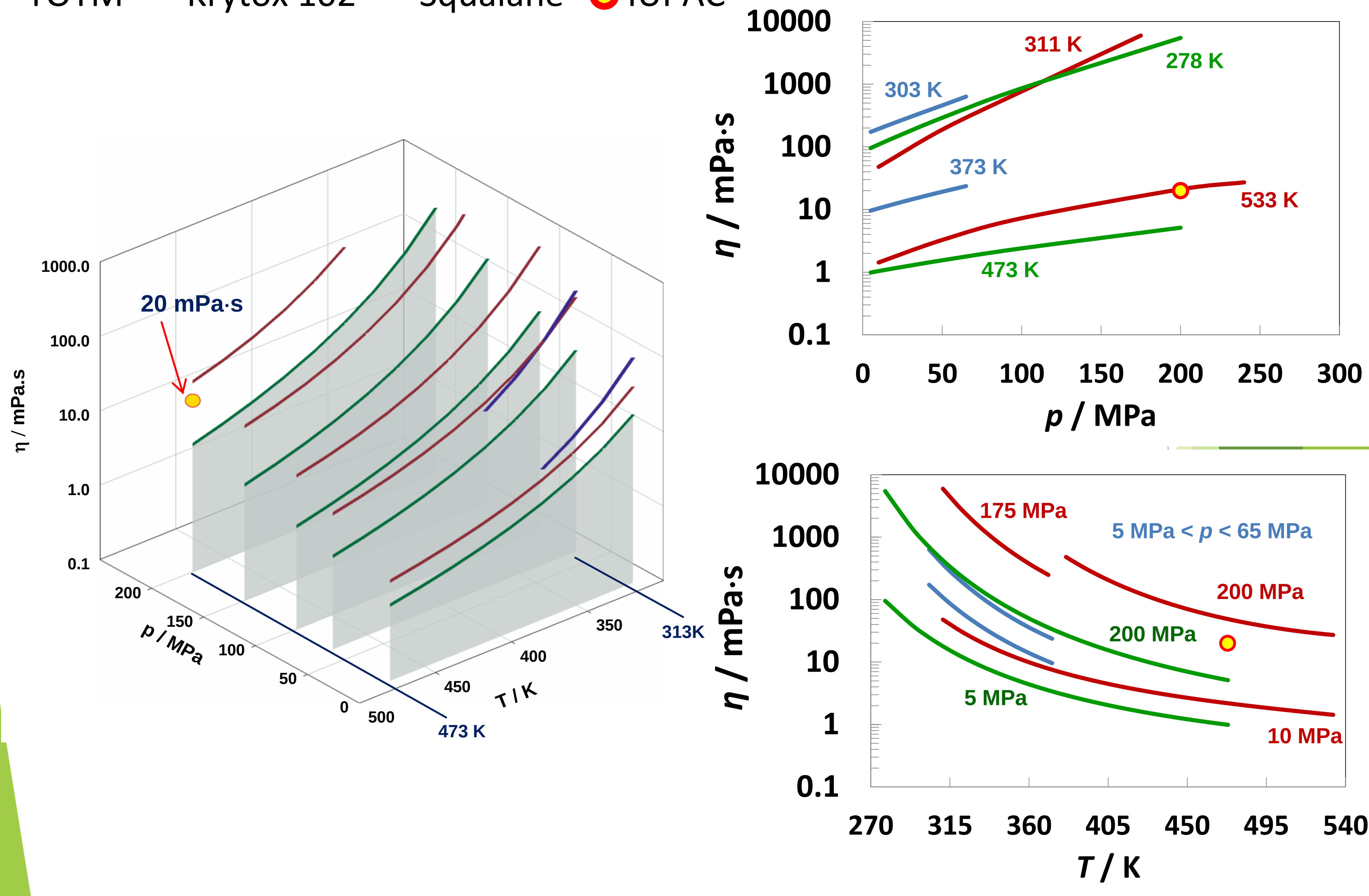
- Potential industrial references for viscosity (comparison with literature)

Liquid		η[a] (mPa.s)	T range (K)	p range (MPa)	η range (mPa.s)	U (%)	Min Purity (%)
Adipates	DMA	3.0	283-373	0.1-20	0.9-4	1	99
	DEA	3.1	283-373	0.1-20	0.9-4.6	1-2	99
	DPA	3.6[b]	303-333	0.1-18	2.0-4.3	2	99
	DBA	4.2[b]	303-373	0.1-65	1.3-8.3	1.5	99
	DIBA	5.3	283-373	0.1	1.3-8.6	1	99
	DEHA	11.4	291-368	0.1	2.1-14.7	--	99
Benzoates	EHB	5.6	263-248	0.1-315	1.7-286.7	2	99
Sebacates	DEHS	17.5	278-373	0.1	2.7-43	1-5.6	98
Squalane		28.2	273-473	0.1-350	0.85-954	1-5	98
Perfluoropolyether	Krytox® GPL 102	32[c]	311-533	0.1-246	1.2-5777	2.4	99.9
Phthalates	DEHP	57.9	273-353	0.1-371	6.2-2555	1-2	99.5
	DINP	55.3	288-368	0.1	4.5-102	--	99
	DIDP	88.5	273-373	0.1-140	5.0-845	0.3-2	99.8
Trimelitates	TOTM	213.4	298-373	0.1-65	9-464	2	99

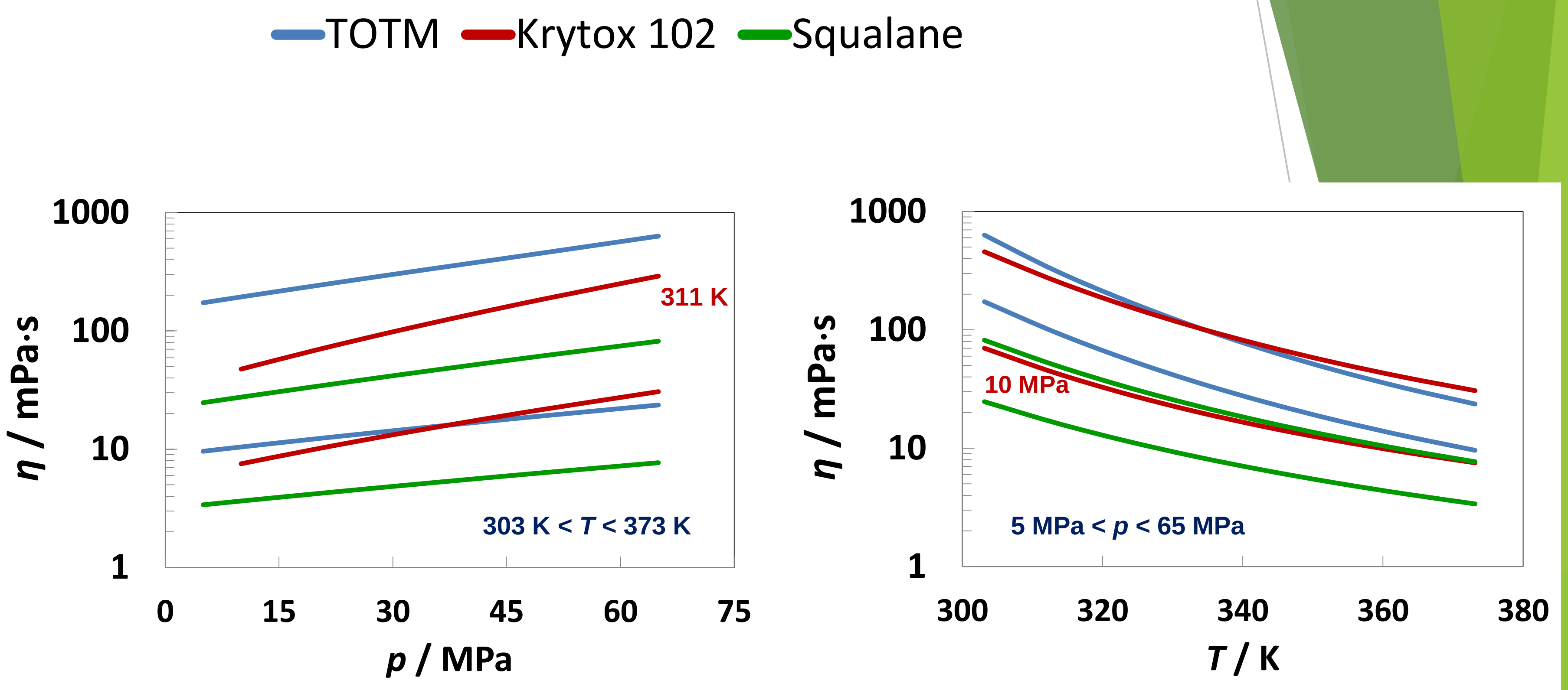
(a) 298 K and 0.1 MPa; (b) 303 K and 0.1 MPa; (c) 311 K and 0.1 MPa

High Pressure High Viscosity Measurements

TOTM Krytox 102 Squalane IUPAC



High Pressure High Viscosity Measurements



IUPAC (473 K; 200 MPa ; 20 mPa·s)

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